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by

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POWERFUL OXIDIZING AGENTS FOR THE OXIDATIVE DEINTERCALATION  
OF LITHIUM FROM TRANSITION METAL OXIDES

Abigail R. Wizansky, Paul E. Rauch,  
and Francis J. DiSalvo, Jr.\*

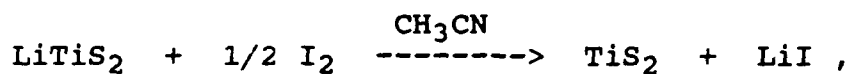
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Abstract.  $\text{NO}_2^+$  and  $\text{MoF}_6$  are shown to be powerful oxidizing agents for the deintercalation of lithium from  $\text{LiCoO}_2$  and  $\text{Li}_2\text{CuO}_2$ . The oxidations, which usually were accompanied by some side reaction, yielded materials of composition  $\text{Li}_x\text{MO}_2$  with  $x \sim 0$  for  $\text{M}=\text{Co}$  and  $x \sim 1.5$  for  $\text{M}=\text{Cu}$ . Both starting materials are insulating ( $\rho > 10^3 \Omega\text{cm}$ ), but the deintercalated products are much more conducting (by at least four orders of magnitude).

## INTRODUCTION

Previous studies of the intercalation chemistry of many transition metal chalcogenide systems have established that  $I_2$  and  $Br_2$  are effective reagents for the oxidative deintercalation of lithium from sulfide and selenide compounds(1). A familiar example of such a deintercalation is the reaction of iodine with  $LiTiS_2$ ,



in which titanium is oxidized from 3+ to 4+. We have been interested in developing lithium deintercalation chemistry as a synthetic route to highly-oxidized transition metal oxides. There are only a few reports in the literature of lithium deintercalation from oxides; these include both chemical oxidation (of  $LiVO_2$  (2),  $LiNbO_2$  (3), and  $LiCoO_2$  (4), using bromine or iodine as oxidizing agent) and also electrochemical oxidation (of  $LiCoO_2$  (5) and  $LiNiO_2$  (6) ). In the reported chemical oxidations with bromine, the removal of lithium did not usually proceed to completion, and we expect that some oxides will require more powerful oxidants than bromine for any reaction to occur at all; thus we have been searching for such oxidants capable of deintercalating lithium from oxides.

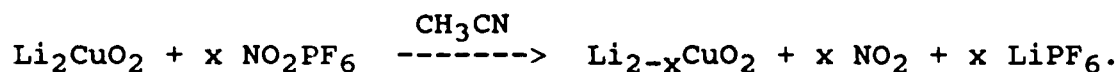
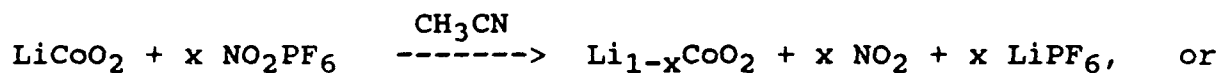
Three potentially useful oxidizing agents are  $NO^+$ ,  $NO_2^+$ , and  $MoF_6$ . Figure 1 shows the estimated redox potentials of the

couples  $\text{NO}^+/\text{NO}$  (7),  $\text{NO}_2^+/\text{NO}_2$  (8) and  $\text{MoF}_6/\text{MoF}_6^-$  (7) in acetonitrile solution, as well as an estimated value for  $\text{PtF}_6/\text{PtF}_6^-$  (9) for comparison. All are at substantially higher potentials than the commonly-used agents  $\text{I}_2$  and  $\text{Br}_2$ . (Note that the  $\text{PtF}_6/\text{PtF}_6^-$  potential is well beyond the oxidative decomposition limit of acetonitrile, which is at approximately +3 volts versus NHE.) Our work has focused around two oxides,  $\text{LiCoO}_2$  and  $\text{Li}_2\text{CuO}_2$ .  $\text{LiCoO}_2$ , which has an ordered rocksalt structure with alternating layers of lithium and cobalt, was chosen to allow comparison with previous deintercalation studies using  $\text{Br}_2$  as the oxidant (4). The main structural feature of  $\text{Li}_2\text{CuO}_2$  (10) is a one-dimensional chain of edge-sharing  $\text{CuO}_4$  square-planar units, with lithium positioned in tetrahedral sites between the chains (see Figure 2). In this previously unexamined case, removal of lithium would formally oxidize the copper from  $2+$  to  $3+$ , possibly changing the insulating  $\text{Cu}^{2+}$  phase into a metal or even a superconductor. While the square-planar  $\text{CuO}_4$  units in  $\text{Li}_2\text{CuO}_2$  are edge-sharing rather than corner-sharing to form chains or sheets as in the recently discovered high- $T_c$  superconductors, the connection between structure and superconductivity in copper oxides has still not been elucidated and it may be useful to search for superconductivity in mixed  $\text{Cu}^{2+}/\text{Cu}^{3+}$  oxides with various structural features.

## EXPERIMENTAL

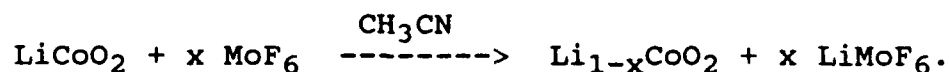
$\text{LiCoO}_2$  was prepared as a black powder by heating  $\text{Li}_2\text{CO}_3$  and cobalt metal in air to 900C for 2d.  $\text{Li}_2\text{CuO}_2$  was prepared as a red-brown powder from  $\text{Li}_2\text{O}_2$  and  $\text{CuO}$  in a platinum crucible under flowing oxygen at 500C for 5d.

The oxidations were carried out in acetonitrile under an argon atmosphere. The source of  $\text{NO}_2^+$  was a soluble hexafluorophosphate salt,  $\text{NO}_2\text{PF}_6$  (Morton Thiokol Alfa). The salt was heated to 100C under vacuum to remove volatile impurities and was then reacted with the oxides:



(The  $\text{LiPF}_6$  is soluble in acetonitrile, while the oxide product remains behind as the only solid phase.) The  $\text{NO}_2^+$  oxidation of  $\text{Li}_2\text{CuO}_2$  was especially vigorous.

Reactions with  $\text{MoF}_6$  were carried out by condensing gaseous  $\text{MoF}_6$  into acetonitrile containing the oxide:



After filtration and drying in vacuo, the oxide powders were

characterized by X-ray powder diffraction and atomic emission (Li) or absorption (Cu) spectroscopy.

## RESULTS AND DISCUSSION

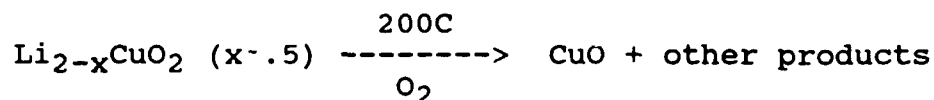
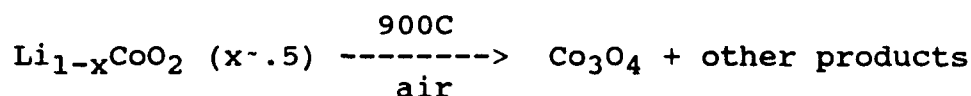
Mizushima et al (5) have examined the X-ray diffraction pattern of  $\text{Li}_{1-x}\text{CoO}_2$  as a function of lithium content. For  $x < .5$  they were able to index all peaks on the hexagonal cell of  $\text{LiCoO}_2$  and to observe gradual changes in the  $c$  lattice parameter by following the position of the (003) line in the diffraction pattern. ( The (003)  $d$ -spacing gives the spacing between  $\text{CoO}_2$  layers.) They noted that for  $x > .67$  diffraction peaks became few and broad. Consistent with their results, we observe from X-ray diffraction that the product  $\text{Li}_{1-x}\text{CoO}_2$  with  $x$  near 1 is highly disordered. When  $\text{LiCoO}_2$  is treated with half an equivalent of  $\text{NO}_2^+$ , the (003) and (104) peaks remain from the powder pattern of the starting material, with slightly shifted  $d$ -spacings; after reaction with a full equivalent of  $\text{NO}_2^+$ , only one peak is visible, in the approximate position of the (003) line of the starting material. Because this peak is consistently observed as the lithium content in  $\text{Li}_{1-x}\text{CoO}_2$  is gradually varied, it seems reasonable to conclude from its presence that the  $\text{CoO}_2$  layer structure is retained and to interpret its position as representing the spacing between  $\text{CoO}_2$  layers. Note that since only a single line is visible in the diffraction pattern of



$\text{Li}_{1-x}\text{CoO}_2$  for  $x$  near 1, the disorder in the structure cannot be just a simple stacking disorder (11), but must also involve irregular spacing of the  $\text{CoO}_2$  layers along the  $c$  axis.

X-ray diffraction results for the copper compound indicate that the material of nominal composition  $\text{Li}_{2-x}\text{CuO}_2$  ( $0 < x < 1$ ) is actually a mixture of two phases: stoichiometric  $\text{Li}_2\text{CuO}_2$  and a new second phase (of approximate composition  $\text{Li}_{1.5}\text{CuO}_2$ ) characterized by 7 broad diffraction peaks (see Table I).

Both the cobalt and copper products are unstable at high temperatures, decomposing as follows:



The oxidation of  $\text{LiCoO}_2$  with  $\text{MoF}_6$  appears to be close to 100% efficient. However, the oxidations with  $\text{NO}_2^+$  of both  $\text{LiCoO}_2$  and  $\text{Li}_2\text{CuO}_2$  involve significant side reaction. During the reaction of  $\text{NO}_2^+$  with  $\text{Li}_2\text{CuO}_2$ , 10% of the  $\text{Li}_2\text{CuO}_2$  decomposes into solution, according to an atomic absorption measurement of the Cu concentration in the acetonitrile reaction solution. Also, elemental analysis of the product  $\text{Li}_{2-x}\text{CuO}_2$  reveals a large

difference between the nominal composition (based on the amount of  $\text{NO}_2^+$  used) and the actual composition:

<u>nominal x in <math>\text{Li}_{2-x}\text{CuO}_2</math></u>	<u>actual value</u>
.50	.25
.75	.42
1.00	.49

Similarly, in the reaction of  $\text{NO}_2^+$  with  $\text{LiCoO}_2$ , some cobalt ends up in solution, as evidenced by the cobalt oxide precipitate which forms on addition of aqueous base to the reaction solution; as with the copper compound, significantly less than one Li is removed for each  $\text{NO}_2^+$  used. Unfortunately, direct elemental analysis of the product  $\text{Li}_{1-x}\text{CoO}_2$  was not possible due to its poor solubility. Also, analysis of the reaction solution for lithium would not give a reliable estimate of the degree of deintercalation since some of the lithium in solution would be due to a destructive side reaction of  $\text{LiCoO}_2$  rather than to deintercalation. In the absence of a direct chemical method for determining the lithium content of the deintercalated samples, we have attempted to monitor the degree of deintercalation with X-ray diffraction by correlating the observed interlayer spacings with the amount of oxidizing agent used. This correlation is summarized in Figure 3, a plot of interlayer spacing versus amount of oxidant used; here the "interlayer spacing" is an average value as measured by the position of the one visible diffraction peak. Data from electrochemical deintercalations by

Mizushima et al (5) have been included on the figure. Since  $\text{NO}_2^+$  is not completely efficient at deintercalation, the  $\text{NO}_2^+$  data points do not overlap the electrochemical or  $\text{MoF}_6$  data; that is, two equivalents of  $\text{NO}_2^+$  are required to achieve maximal deintercalation. The observed increase in the interlayer spacing with decreasing lithium content is somewhat unusual in that such spacings usually decrease on deintercalation. A similar increase was observed by Mendiboure et al (4) in an electrochemical deintercalation of  $\text{LiCoO}_2$ .

Two-point resistance measurements were obtained on pressed powders in an argon-filled glove box. Calculated resistivities for the cobalt compounds are  $5.4 \times 10^3 \Omega\text{cm}$  for  $\text{LiCoO}_2$  and  $.6 \Omega\text{cm}$  after reaction with one equivalent of  $\text{NO}_2^+$ ; in the copper system, the resistivity is greater than  $10^6 \Omega\text{cm}$  for  $\text{Li}_2\text{CuO}_2$  but drops to  $71 \Omega\text{cm}$  upon reaction with one equivalent of  $\text{NO}_2^+$ . Both compounds show a drop in resistivity of four or more orders of magnitude upon oxidation. While such measurements cannot be trusted for quantitative comparison due to the importance of interparticle contact resistance, the large decrease in resistivity clearly indicates that the products are more conducting than the reactant solids. Dc magnetic susceptibility measurements show that the product oxides are not superconducting down to 4K.

In summary, we report here the use of the powerful oxidizing agents  $\text{NO}_2^+$  and  $\text{MoF}_6$  to deintercalate lithium from transition metal oxides. Although with some oxides side reaction can be significant, these and similar chemical oxidants may provide an

effective low temperature route to the synthesis of highly-oxidized transition metal oxides.

Acknowledgements. We thank J. M. Shreeve of the University of Idaho for her generous donation of the  $\text{MoF}_6$ . Support for this work through the Office of Naval Research is gratefully acknowledged. Also, ARW has been supported in this work by a National Science Foundation Graduate Fellowship.

## REFERENCES

1. See, for example, D.W. Murphy and P.A. Christian, *Science* 205(4407), 651 (1979).
2. K. Vidyasagar and J. Gopalakrishnan, *J. Solid State Chem.* 42, 217 (1982).
3. N. Kumada, S. Muramatu, F. Muto, N. Kinomura, S. Kikkawa and M. Koizumi, *J. Solid State Chem.* 73, 33 (1988).
4. A. Mendiboure, C. Delmas and P. Hagenmuller, *Mater. Res. Bull.* 19, 1383 (1984).
5. K. Mizushima, P.C. Jones, P.J. Wiseman and J.B. Goodenough, *Mater. Res. Bull.* 15, 783 (1980).
6. J.B. Goodenough, K. Mizushima and T. Takeda, *Jpn. J. Appl. Phys.* 19 Supplement 19-3, 305 (1980).
7. G.M. Anderson, J. Iqbal, D.W.A. Sharp, J.M. Winfield, J.H. Cameron and A.G. McLeod, *J. Fluorine Chem.* 24, 303 (1984).
8. Estimated from the value for  $\text{NO}^+/\text{NO}$  given in reference 7 together with the ionization enthalpies for NO and  $\text{NO}_2$  given by F.A. Cotton and G. Wilkinson in "Advanced Inorganic Chemistry" 4th edition, pp. 424-426, John Wiley and Sons, New York (1980).
9. Estimated from the values for  $\text{MoF}_6$  and  $\text{WF}_6$  given in reference 7 together with the estimated difference in electron affinities of  $\text{WF}_6$  and  $\text{PtF}_6$  given by N. Bartlett in *Angew. Chem. Int. Ed. Engl.* 7(6), 433 (1968).
10. R. Hoppe and H. Rieck, *Z. anorg. allg. Chemie* 379, 157 (1970).
11. See, for example, A. Guinier, "X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies" Section 7.2, W.H. Freeman and Company, San Francisco (1963).

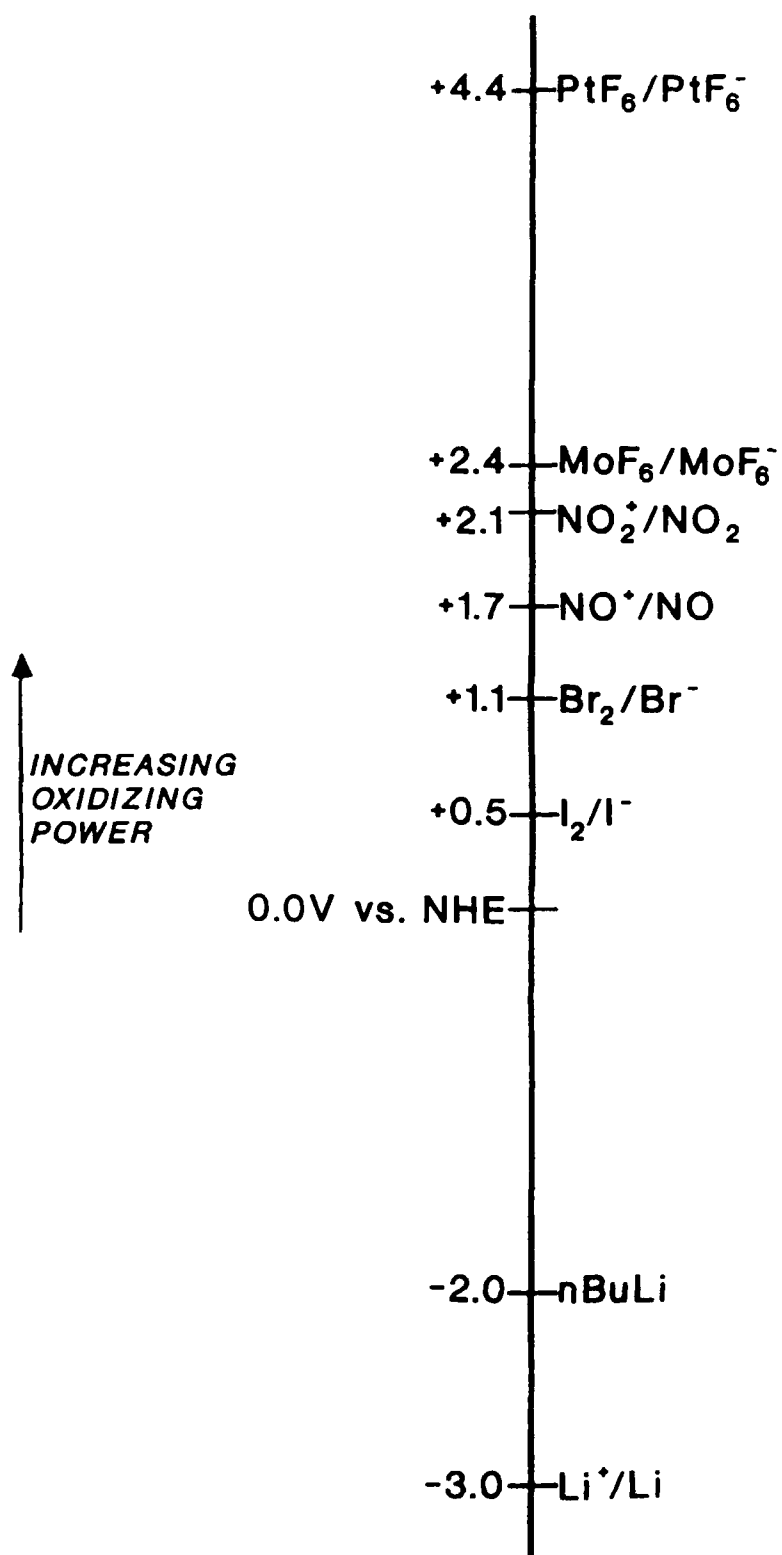
Table I. X-ray powder data for the product of the reaction of  $\text{Li}_2\text{CuO}_2$  with one equivalent of  $\text{NO}_2\text{PF}_6$ .

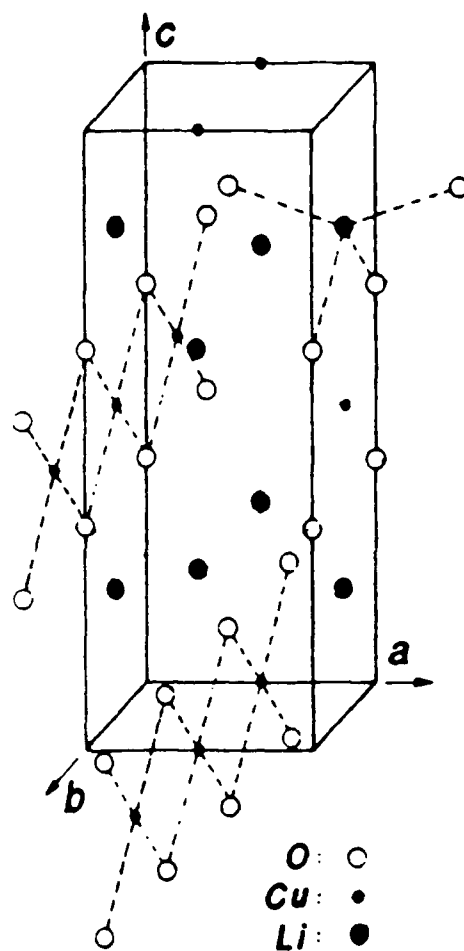
<u>d (Å)</u>	<u>estimated intensity</u>
4.84	100
3.58	30
2.87	50
2.78	25
2.47	25
2.13	40
1.95	50

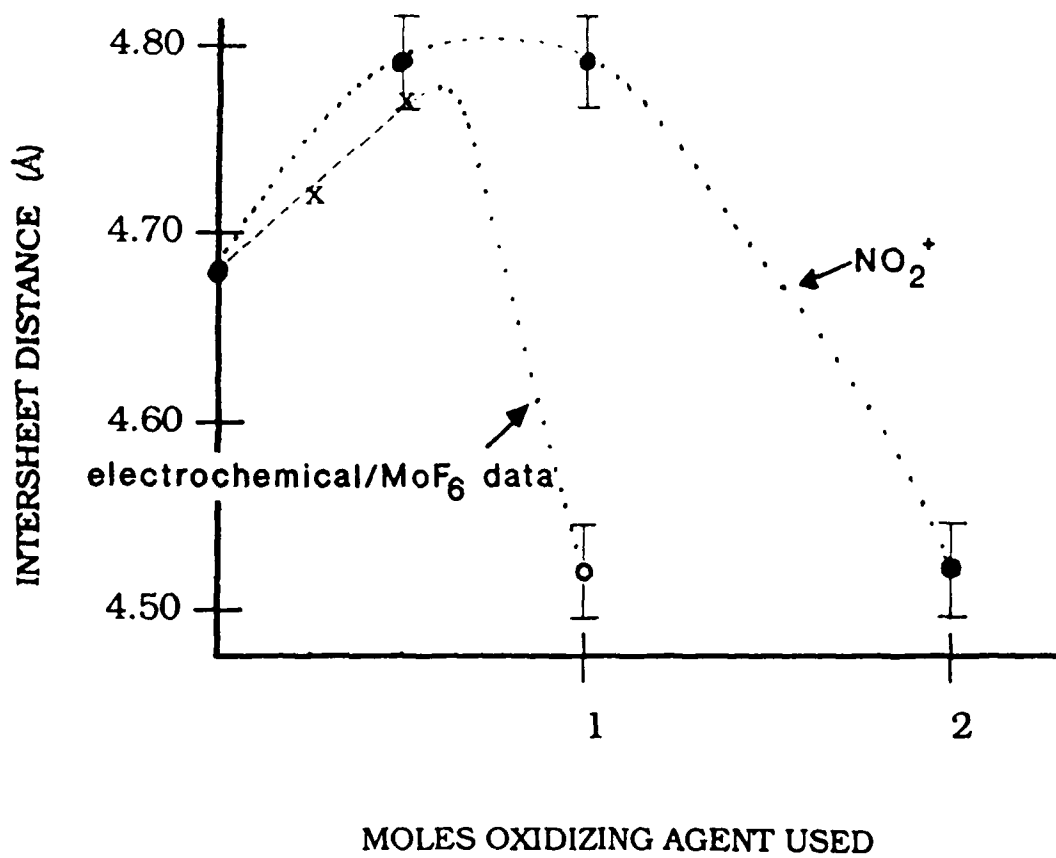
## FIGURE CAPTIONS

- Figure 1. Estimated redox potentials in acetonitrile. After a similar figure from reference (1).
- Figure 2.  $\text{Li}_2\text{CuO}_2$  unit cell. Shows one-dimensional chains of edge-sharing  $\text{CuO}_4$  units;  $\text{Li}_2\text{CuO}_2$  crystallizes in the orthorhombic space group  $\text{Immm}$  with  $Z=2$ ,  $a=3.66$ ,  $b=2.86$ , and  $c=9.39$  (crystallographic data is from reference (10) ).
- Figure 3. X-ray diffraction results for  $\text{Li}_{1-x}\text{CoO}_2$ : intersheet distance versus amount of oxidant used.  $x$  = electrochemical deintercalation data from reference (5);  
● =  $\text{NO}_2^+$  data; ○ =  $\text{MoF}_6$  data.









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